

Lastly, in the rhipidoglossate Gastropods, there is a cæcum but apparently no sac.

In conclusion, it would therefore appear that the so-called gizzard of *Spirula* and *Nautilus*, and consequently the similar organ which appears in other Cephalopods, is in reality the homologue of the style-sac of the Gastropods and the Lamellibranchiata. That in the Cephalopods only that portion of the gastric tube which lies between the orifice of the cesophagus and the intestine is the true stomach and consequently comparable to the true stomach of the Gastropods, while, lastly, the valvular diverticulum in relation to the "bile duct" in the Cephalopods is unquestionably the homologue of the similarly related and so-called spiral cæcum which projects from the true stomach of the Gastropods.

"Coefficients of the Cubical Expansion of Ice, Hydrated Salts, Solid Carbonic Acid, and other Substances at Low Temperatures." By JAMES DEWAR, M.A., D.Sc., LL.D., Jacksonian Professor, Cambridge University, and Fullerian Professor, Royal Institution, London. Received April 16,—Read May 1, 1902.

The apparent specific gravities of boiling liquid oxygen which resulted from weighing in the liquid a series of metals and other substances were given in a lecture entitled "New Researches on Liquid Air," printed in the Royal Institution 'Proceedings' for 1896. For instance, silver, calc spar, rock crystal, and iodide of silver gave the respective apparent densities 1·1278, 1·1352, 1·1316, and 1·1372. On correcting the weight of liquid displaced by each substance for contraction to  $-182^{\circ}6$ —by calculating a Fizeau mean coefficient of expansion for the range of temperature employed, on the assumption that the parabolic formula might be legitimately extended to low temperatures,—it was found that the real density of liquid oxygen so deduced for all the bodies used was, as a mean, 1·137.

The determination of the densities of substances at the temperature of the boiling-point of oxygen,—and hence of their mean coefficients of expansion between that temperature and ordinary temperatures,—opens out a very large field of investigation, from which, if a sufficiently large number of observations were available, valuable deductions might be drawn. On account, however, of the expense and trouble of producing quantities of liquid oxygen, its use for this purpose is not likely to become general, although, when available, it is the easiest body to use in conducting such experiments, especially when the vacuum vessel containing it is immersed in a larger vessel containing the same fluid or well evaporated air. The ease with which liquid

air can now be obtained in many laboratories suggests that its application to work of this kind would in some cases be a convenience, and the present investigation was undertaken with the desire of ascertaining what accuracy could be attained, and how the method could be applied to inorganic or organic substances which occur in the form of fine crystals. The use of a mixture of varying composition and density like liquid air necessitates a determination of its density with accuracy and rapidity before and during the course of the experiments. For this purpose, in the experiments about to be detailed, the liquid air that had been allowed to evaporate for twenty-four hours in advance was used in large silver-coated vacuum vessels of some 3 litres capacity. In order to ascertain the density of the liquid, a polished silver ball, which had been weighed once for all in liquid oxygen, was weighed in the sample of liquid air, and from the relative weights thus found the density of the liquid air could be approximately determined, assuming that of liquid oxygen to be  $1.137$ .\* To prevent any disturbing ebullition in the liquid-air flask in which the weighings took place, and to reduce the rate of its evaporation to a minimum during the course of an experiment, the substance to be used was previously cooled in a supplementary vessel containing liquid air and then transferred to the large flask. To avoid as far as possible the formation of cracks in the bodies during the process of immersion in the liquid air, it was found advisable to cool them slowly in the air of the vacuum flask first, and then to lower them into the liquid. In this way, with proper care and attention, results were obtained comparable in accuracy with the density taken in liquid oxygen. Substances like solid carbonic acid and ice were weighed in the cool, gaseous air of the vacuum vessel, and their weights subsequently corrected for buoyancy. The temperature of the densest and lightest samples of liquid air were ascertained by the hydrogen thermometer, and that of the others deduced by graphic interpolation. As the entire range of temperature through which the bodies were cooled amounted to about  $200^{\circ}$ , a degree or two up or down has no real influence on the results; the extreme range of temperature in the air samples was from  $83^{\circ}.8$  to  $86^{\circ}.1$  Abs.

When the body to be examined was a salt, it was employed in the form of a compressed block. One experiment was, however, made in a section of a large crystal of chrome alum. The salt, previously reduced to a fine powder, was moistened with water and compressed in a cylindrical steel mould under great hydraulic pressure. During compression the saturated salt solution drained away, and finally a cylindrical block of some 50 grammes of the salt was obtained free from porosity and hard enough to allow its surface to be polished. In

\* As the correction due to the contraction of the silver ball between the temperature of boiling oxygen and that of the air sample is small, it may be neglected.

this form salts and other materials similarly treated are especially adapted for accurate specific gravity determinations. After such treatment it was found that all the mechanically attached water was got rid of in the case of hydrated salts, and also in such as did not combine with water. In order to get cylindrical blocks of the salts showing no porosity the presence of water, or rather the saturated salt solution, was found to be essential during the application of pressure. In the same way it was found to be an advantage in compressing such a substance as solid carbonic acid, to moisten it with a fluid like ether before applying the hydraulic pressure.

Recalling the work of Playfair and Joule,\* which originated in a suggestion of Dalton's that the volume of a hydrated salt in solution was simply the volume of the water of crystallisation, ice and some hydrated salts were selected, as well as some other bodies whose coefficients of expansion they had determined. Substances of special interest were included in the list, like mercury, sulphur, iodine, and solid carbonic acid, the latter being particularly important as an example of a solidified gas.

In the further conduct of an experiment the observations made on a substance were three, namely: (A) the weight in grammes of the substance and suspending platinum wire, either in air of about 17° C. temperature or in the gaseous air in the flask containing the liquid air; (B) the weight in grammes of the body and wire when immersed in the liquid air; and (C) the weight in grammes of the suspending platinum wire in ordinary (17°) air. This wire was bent into the form of a small cage, to hold the compressed cylinder or portion of the substance to be examined. (C) was measured once for all for each cage, and in the different cases varied from about 0.2 to 0.3 gramme. The relative portion of wire not immersed in liquid air was so small that no appreciable error will be made in (B) by considering that the whole of the wire was immersed. Further, no allowance is made for the (17°) air displaced by the weights themselves. The observed weights A, B, C are therefore connected with the weights and specific gravities of the substances concerned by the very approximate relations

$$A = W + w - \frac{W}{S}d - \frac{w}{s}d,$$

$$B = W + w - \frac{W}{S}D - \frac{w}{s}D,$$

$$C = w - \frac{w}{s}d,$$

\* "Researches on Atomic Volume and Specific Gravity," 'Chem. Soc. Jour.,' vol. 1, 121.

where  $W$  = true weight of substance examined,

$w$  = true weight of platinum wire,

$S$  = specific gravity of substance required,

$D$  = specific gravity of liquid air, when  $B$  was observed,

$d$  = specific gravity of gaseous air when  $A$  was observed,

$s$  = specific gravity of platinum.

From these relations we derive

$$S = \frac{A - C - B \frac{d}{D} + C \frac{d}{D} \frac{s - D}{s - d}}{A - B - C \frac{D - d}{s - d}} D,$$

instead of which we may write

$$S = \frac{A - C}{A - B} D \times \text{correcting factor}.$$

The correcting factor is

$$\frac{1 - \frac{d}{D} \frac{B - C \frac{s - D}{s - d}}{A - C}}{1 - \frac{D - d}{s - d} \frac{C}{A - B}},$$

which in the present circumstances differs from unity only by a few units on 10,000.

In the subjoined Table I are given the values of  $A - C$ ,  $A - B$  and  $D$  for each observation.

In the case of substances of less density than liquid air, a polished copper ball weighing about 38 grammes was used as a sinker. The details of the ice experiments, three in number, are given in Table II.

Two experiments were made on compressed cylinders of solid carbonic acid. In the first of these the carbonic acid was compressed dry, in the second, after a few drops of ether were added. The specific gravities of solid mercury, iodine, and sulphur were also determined in liquid air. The iodine was in the form of a compressed cylinder, but the sulphur was a piece of a crystalline mass of native origin.

The specific gravity of the actual portion of the substance weighed in the liquid air was, with one or two exceptions, determined also at the temperature of the laboratory, about  $17^{\circ}\text{C}$ . From the two sets of observations the value of the mean coefficient of cubical expansion between  $17^{\circ}\text{C}$ ., and the temperature of liquid air, was calculated.

In calculating coefficients of expansion, various forms may be given to the formula employed, and correspondingly different results may be obtained from the same set of observations. For short ranges of temperature these results are practically identical, but this no longer holds for a range of temperature such as we have in these experiments.

All that is possible in the present instance is to adopt a linear formula. The usual formula is  $v_T = v_0 (1 + \alpha T)$ , where the value  $v_0$  at  $0^\circ \text{C.}$  becomes  $v_T$  at  $T^\circ \text{C.}$  when  $\alpha$  is the coefficient of expansion. If we use densities ( $d$ ) instead of volumes ( $v$ ) this formula becomes

$$d_0 = d_T(1 + \alpha T), \quad \text{or} \quad \alpha = \frac{d_0 - d_T}{T d_T}; \quad \alpha = 0.000538.$$

Another formula, when  $T$  and  $T'$  are the temperatures dealt with, is

$$d_T = d_{T'} \{1 + \alpha (T' - T)\}, \quad \text{or} \quad \alpha = \frac{d_T - d_{T'}}{(T' - T) d_{T'}}; \quad \alpha = 0.000595.$$

Again

$$d_{T'} = d_T \{1 - \alpha (T' - T)\}, \quad \text{or} \quad \alpha = \frac{d_T - d_{T'}}{(T' - T) d_T}; \quad \alpha = 0.000558.$$

Also we may choose a mean formula

$$\alpha = \frac{d_T - d_{T'}}{(T' - T) \frac{d_T + d_{T'}}{2}}; \quad \alpha = 0.000576.$$

The differences in the results of applying these formulæ are shown in the numerical values attached to each, which are calculated from the first experiment on solid carbonic acid in Table III, coupled with the specific gravity 1.53 of the solid at  $-78^\circ \text{C.}$

Perhaps as a matter of general convenience, the first of these formulæ is the best; however, the second was chosen to conform with the old work of Playfair and Joule, and it is the results of this formula which appear in the table.

The temperature range is taken from about  $-186^\circ \text{C.}$  to  $17^\circ \text{C.}$ , unless otherwise stated.

*Ice.*—In determining the density at the temperature of liquid air of pieces of clear ice cut from large blocks, both the silver and copper balls already referred to were used as indicated. The true weight *in vacuo* of the silver ball was 132.2855 grammes, and that of the copper ball was 38.0802 grammes. The observations and results are given in Table II. The mean of the three densities at  $-188.7^\circ \text{C.}$  is 0.92999.

Recently Vincent\* has redetermined the density of artificial ice at the freezing-point, and also its coefficient of expansion. He finds the density to be 0.916, or from his tabulated results 0.91599. Playfair and Joule find the mean of the densities given by eight observers previous to them, to be 0.919, and they themselves get 0.9184; Bunsen found it to be 0.9167. If we take this most recent determination, namely, 0.91599 at  $0^\circ$ , and 0.92999 at  $-188.7^\circ$ , and use the formula

$$d_0 = d_T(1 + \alpha T)$$

we get  $\alpha = 0.00008099$ .

\* 'Roy. Soc. Proc.,' 1901.

Vincent refers to "only one" estimate for natural ice, namely, 0·0001125, adding that "the mean of three available results for artificial ice is 0·000160"; finally, he gives the mean of four determinations of his own, namely, 0·000152. Apparently then, we may take 0·0001551 as the mean coefficient of expansion of ice between 0° and (say) -20° C. Thus the mean coefficient of expansion between 0° and -188° C. is about half of that between 0° and -20° C. The mean coefficient of expansion of water in passing from 4° to -10° is -0·000362, and from 4° to 40° C. it is 0·0002155. Hence the mean coefficient of expansion of ice between 0° and -188° C., is about one-fourth of that of water between 0° and -10° C., and half of that between 4° and 100° C.

If we had the densities of ice at still lower temperatures, the values of the coefficient of expansion thence determined would, we have every reason to believe, be less than what we have found. We shall therefore not be overstraining the argument if we use the value just found to determine an upper limit to the density of ice at the absolute zero. The result is 0·9368, corresponding to a specific volume 1·0675. Now the lowest density of water, namely, at the boiling-point, is 0·9586 (corresponding to specific volume 1·0432), so that ice can never be cooled low enough to reduce its volume to that of the liquid taken at any temperature under one atmosphere pressure. In other words, ice molecules can never be so closely packed by thermal contraction as the water molecules are in the liquid condition, or the volume of ice at the absolute zero is not the minimum volume of the water molecules. It has been observed by Professor Poynting\* that if we suppose water could be cooled without freezing, then taking Brunner's coefficient for ice, and Hallstrom's formula for the volume of water at temperatures below 4° C., it follows that ice and water would have the same specific volume at some temperature between -120° and -130°; applying the ordinary thermodynamic relation, then no change of state between ice and water could be brought about below this temperature. On the other hand, Clausius† has shown that the latent heat of fusion of ice must be lowered with the temperature of fusion some 0·603 of a unit per degree. If such a decrement is assumed to be constant, then about -130° the latent heat of fluidity would vanish.‡ Baynes discusses the same subject,§ and arrives at the conclusion that at a temperature of -122°·8 C. and under a pressure of 16,632 atmospheres

\* "Change of State, Solid, Liquid," 'Phil. Mag.,' 1881.

† 'Mechanical Theory of Heat,' p. 172 (1879).

‡ In my paper "On the Lowering of the Freezing-point of Water by Pressure," 'Roy. Soc. Proc.,' 1880, it was proved that up to 700 atmospheres the rate of fall was constant and equal to the theoretical value within the range of pressure if the difference between the specific volumes of ice and water remain constant; thence the latent heat of fusion must diminish just as Clausius had predicted.

§ 'Lessons on Thermodynamics,' p. 169 (1878).

there is no distinction between the solid and liquid forms of water. At temperatures below this limit no amount of pressure would transform ice into water. We are thus relieved from a difficulty that would follow but for this demonstration of Clausius, namely, that the application of enormous pressures to ice, even at temperatures below that of liquid hydrogen, might cause the transformation of ice into water.

*Carbonic Acid.*—Two experiments were made with this substance, the masses in each case being about 20 grammes. These were compressed cylinders; the former was compressed dry, while the latter was slightly moistened with ether. The data and results are given in Table III.

The density of solid carbonic acid at its boiling-point was formerly given as 1·5,\* but the mean of my results at the time came to 1·53. Recently the same value has been found by Behn. Taking this value and 1·6267, the mean of the above results at  $-188^{\circ}8$  C., and using the formula  $d_T = d_{T'}\{1 + \alpha(T' - T)\}$  we get  $\alpha = 0.0005704$ .

This is a very large coefficient of expansion, being greater than that of any substance recorded in Table I, and comparable with that of sulphur between  $80^{\circ}$  and  $100^{\circ}$ , which, according to Kopp, is 0·00062. The coefficient of liquid carbonic acid at its melting-point taken from the recent observations of Behn† is 0·002989, so that the rate of expansion of the liquid at its smallest value is very nearly five times that of the solid.

*Solid Mercury.*—One experiment was made with solid mercury, of which the details are given in Table I.

Mallet determined with great accuracy the density of solid mercury at  $-38^{\circ}85$ , his result being 14·193; coupling this with the density found for the liquid-air temperature, we find the value of the coefficient of expansion between the melting-point and  $-189^{\circ}$  C. is 0·0000887. For fluid mercury above  $0^{\circ}$  C. the mean value is about 0·000182, so that in the solid state this coefficient is about half of that in the fluid state.

#### *Notes on the Results of Table I.*

Sodium, extending down to low temperatures, has a coefficient about the same as that of mercury at the ordinary temperature. The coefficient for sulphur is about half of that between  $0^{\circ}$  and  $100^{\circ}$ , being 0·0002237, and that of iodine is not far removed from the value 0·000285 given for the solid at ordinary temperatures. The rate of expansion of liquid iodine is about three times this value. Paraffin ought to have a value of 0·0004633 from Fizeau, but Rodwell's coefficient between  $0^{\circ}$  and  $38^{\circ}$  is 0·00035. The value found for

\* See 'Proc. Roy. Inst.,' 1878, "The Liquefaction of Gases."

† 'Chem. Jour.,' 1901.

Table I.

	A-C.	A-B.	D.	$d, \dagger$	$d_{17}$	$\alpha$ 0.000.
Sulphate of aluminium (18)*.	45.338	26.961	1.0225	1.7194	1.6913	0811
Biborate of soda (10).	47.037	28.328	1.0405	1.7284	1.6987	1000
Chloride of calcium (6)	68.942	37.493	0.9347	1.7187	1.6775	1191
Chloride of magnesium (6)	36.663	22.438	0.9816	1.6039	1.5693	1072
Potash alum (24)	50.462	30.177	0.9816	1.6039	1.6144	0813
Chrome alum (24), large crystal	47.345	26.406	1.0226	1.8385	1.8199	0365
"	40.147	23.665	1.0517	1.7842	1.7669	0478
Carbonate of soda (10)	55.675	34.863	0.9347	1.4926	1.4460	1563
Phosphate of soda (12)	57.085	35.848	0.9700	1.5446	1.5200	0787
Hyposulphate of soda (5)	53.121	28.836	0.9573	1.7655	1.7290	0069
Ferrocyanide of potassium (3)	55.914	29.115	0.9887	1.8988	1.8533	1195
Ferri cyanide of potassium	68.902	35.961	0.9837	1.8944	1.8109	2244
Nitro-prusside of sodium (4)	49.614	28.526	0.9887	1.7196	1.6803	1138
Chloride of ammonium, sample i.	34.530	21.032	0.9597	1.5757	1.5188	1820
"	31.083	18.870	0.9597	1.5809	1.5216	1893
Oxalic acid (2)	23.614	13.293	0.9571	1.7024	1.6145	2643
Oxalate of methyl	56.465	37.760	1.0217	1.5278	1.4260	3482
Paraffin	15.675	16.031	0.9992	0.9770	0.9103	3567
Naphthalin	43.622	33.001	0.9347	1.2355	1.1589	3200
Chloral hydrate	53.321	26.436	0.9789	1.9744	1.9151	1482
Urea	42.811	32.326	1.0282	1.3617	1.3190	1579
Iodoform	140.012	32.381	1.0282	4.4443	4.1955	2980
Iodine	17.806	4.135	1.137	4.8943	4.6631	2510
Sulphur	25.499	13.813	1.137	2.0989	2.0322	1152
Mercury	77.719	5.135	0.9502	14.382	14.193†	0887
Sodium	16.904	16.504	0.9818	1.0066	0.972	1865
Graphite (Cumberland)	22.221	9.986	0.9573	2.1302	2.0990	0733

\* The figures ( ) refer to the number of molecules of water of crystallisation. † Density at the temperature of liquid air. ‡ At  $-38^{\circ}\text{C}$ .



naphthalin is about half that of the liquid near its melting-point, viz., 0·000785. If the liquid coefficient be taken at a corresponding temperature to that of the liquid carbonic acid when comparing it with the solid, then its value is 0·001213, or the coefficient would be now in the ratio of 4 to 1. The graphite calculated from Fizeau should be 0·0000929, which is greater than my value; but the samples were different. My two specimens of chloride of

Table II.—Ice.

Silver ball. Weight lost in (1) oxygen, (2) liq. air.	Density of liquid air.	Weight of ice and copper ball and wire.		Weight of copper ball and wire.		Weight of ice <i>in vacuo</i> .	Density of ice at -188°·7 C.
		Gaseous air at -188°·7 C.	Liquid air at -188°·7 C.	Air at 16° C.	Liquid air -188°·7 C.		
(1) 14·411 (2) 12·446	0·9820	47·080	33·430	38·075	33·933	9·0612	0·93032
(1) 14·409 (2) 12·042	0·9502	46·78	33·88	38·128	34·103	8·706	0·92646
(1) 14·407 (2) 12·597	0·9942	56·391	32·740	38·127	33·94	18·167	0·93318

Table III.—Solid Carbonic Acid.

Weight of solid CO <sub>2</sub> .		Density of liquid air.	Weight <i>in vacuo</i> .	Density at at -188°·8 C.
Gaseous air at -188°·8 C.	Liquid air at -188°·8 C.			
19·865	7·905	0·9832	19·919	1·6308
22·55	9·37	0·9502	22·61	1·6226

ammonium gave nearly the same value, and the result is in agreement with that found by Playfair and Joule, viz., 0·000191. If a Fizeau coefficient for this salt is calculated, the value is 0·0000761, which in this case is far too small. The coefficient found for oxalic acid is again only a little smaller than that given by Playfair and Joule, viz., 0·0002748. As regards the hydrated salts, phosphate of soda, hypo-sulphate of soda, and chloride of calcium, having the respective values 0·0001384, 0·0001516, and 0·0006887, as found by Kopp, the low tem-

perature coefficients are much smaller in each case. With the exception of carbonate of soda and chrome alum, all the other hydrated salts have a coefficient of expansion not differing greatly from that of ice at low temperatures. Generally, the densities of the compressed blocks of different bodies agreed well with the results of other observers, but my potash alum had only a density of 1·614, whereas Playfair and Joule give 1·731. It will be noted that iodoform is a highly expansive body like iodine, and that oxalate of methyl has nearly as great a coefficient as paraffin, which is one of the most expansive solids. The correcting factor was used for paraffin, naphthalin, chloral hydrate, iodoform, and sodium. All weights are in grammes.

It will be possible by cooling the moulds with liquid air during the process of hydraulic compression, to produce cylindrical blocks of solid bodies of lower melting-points than any given in this investigation, such as alcohol, ether, nitrous oxide, ammonia, chlorine, &c., and to ascertain their coefficients of expansion in the solid state between the individual melting-points and the boiling-point of liquid air.

This method, which works well with liquid oxygen or air, fails when applied to liquid hydrogen, as the density of the liquid is too small (apart from other difficulties) to give accurate values of the weights of fluid displaced. For temperatures about 20° absolute, recourse must be had to measurements of the coefficient of linear expansion, and such observations could only be applied with ease to metallic bodies and alloys.

“Report of Absolute Magnetic Observations at the Valencia Observatory (Cahirciveen, co. Kerry), 1899, 1900, and 1901.”

By J. E. CULLUM. Communicated by The EARL OF ROSSE, F.R.S. Received April 12,—Read April 24, 1901.

As far back as 1887 the late Professor FitzGerald, of Trinity College, Dublin, expressed a desire for a series of magnetic observations to be made in Ireland, when the writer offered to undertake the work if he was provided with instruments, and obtained the consent of the Meteorological Council. This was done, and an old pattern unifilar by Jones, with a dip circle by Barrow, being loaned by Trinity College, experimental observations were commenced in a wooden hut erected in the Observatory grounds in Valencia Island, with funds supplied by the Royal Irish Academy. The result of the first few years of this series was published in the ‘Proceedings of the Royal Irish Academy,’ and the observations were continued until the end of 1896. The observatory was removed in 1892 to Cahirciveen, about 4 miles eastward.